

# Aluminum Electrochemical Deposition and Its Microsystem Applications

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## 論文内容要約

Aluminum (Al) has played a significant role in various aspects of human life. It has been the most heavily used and the most abundant nonferrous metallic material on earth. Its metal and alloys are being utilized for a wide variety of applications owing to their excellent properties and affordability, starting from home appliances, building industries, transportation and even some smaller components: microelectronics and microsystems (or MEMS, micro electro mechanical system). However, the exploration of the material in microelectronics and microsystems has been constrained to its thin film due to the inability to deposit its thick film of several  $\mu\text{m}$  with a high efficiency. In microelectronics and microsystems, Al is generally deposited by physical vapor deposition techniques, either evaporation or sputtering method. Such methods have enabled the formation of a dense and uniform film with high purity. However, both techniques exhibit a limited deposition rate in the order of several 10 nm/min. Such a low deposition rate has prevented the film to grow to a relatively high thickness of several  $\mu\text{m}$  or beyond. Meanwhile, the PVD techniques are not developed for selective deposition. Film patterning steps using either lift-off or etching method is required to form structures using the film. However, such steps are not suitable for thick film structures because a large portion of the deposited film is wasted.

A molded electrochemical deposition method has been widely employed to form thick microstructures with high aspect ratio in microelectronics and microsystems. The process is selected mainly due to its rapid deposition rate and its ability to deposit selectively only on the desired area. Meanwhile, the process also offers controllability over the material properties of the resulting deposit by tuning the deposition parameters. Such flexibility has enabled the users to design the material to have their desired properties depending on the application. The recent development of Al electrochemical deposition using an ionic liquid as the solvent is a promising technology to break the limitation in depositing a thick Al for microsystems. However, the main direction of the studies regarding Al electrochemical deposition has been towards an anti-corrosion coating application. Therefore, this study aims to pave the way for the microsystem applications of the electrochemically deposited Al film.

The electrochemical deposition process is well known to offer controllability over various properties of the resulting deposit. To practically employ an electrochemically deposited Al film in microsystems, firstly its material properties and the influence

of different deposition conditions have to be elucidated. In addition, to improve the surface morphology of the electrochemically deposited Al, various additives have been introduced in previous studies. However, their influence on the material behavior of the deposit is still unknown despite its importance for designing microsystems. In this study, microstructure, mechanical, electrical and thermal properties of Al film electrochemically deposited from a chloroaluminate ionic liquid electrolyte with the absence and presence of an additive were comprehensively investigated. A mixture of  $\text{AlCl}_3$  and a chloroaluminate ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) was selected due to its promising properties for Al electrochemical deposition, owing to its ability to maintain the liquid state over a wider composition range, lower viscosity and relatively wider electrical potential window. An organic salt compound 2-chloronicotiny chloride was selected as the additive in this study due to its ability to form a uniform Al deposit in previous studies and its less potential damage to the photoresist mold which will be required for microstructuring of the film. The microstructures of the deposits were comprehensively studied by cross-sectional scanning electron microscope (SEM), transmission electron microscope (TEM) and electron backscatter diffraction (EBSD) spectroscopy. In the absence of the additive, the elastic modulus and nanoindentation hardness of the film varied between 41–102 GPa and 486–908 MPa, respectively, depending on the deposition parameter. The electrical resistivity and the coefficient of thermal expansion of the deposits varied between 51–160  $\text{nm } \Omega$  and 2–20 ppm/K, respectively, depending on the deposition parameter. The presence of the additive also drastically improved the surface roughness and nanoindentation hardness by factors of about 100 and 3, respectively. The additive inclusion inhibited the grain growth in the in-plane direction of the film. The residual stress was found to be highly controllable by the deposition bath temperature. The electrical resistivity at the presence of the additive was measured as about 100  $\text{nm } \Omega$ . The characterized properties were associated to the microstructures of the deposits, which can be tailored by adjusting the deposition conditions. The evolution of the material properties obeyed the well-known Hall-Petch relation in its hardness. The electron scattering at the grain boundary also influenced the electrical resistivity, as the film with finer grain exhibited higher electrical resistivity. The obtained knowledge is useful as a design guide for the future applications of the film.

The electrochemical deposition process has been widely used to deposit a relatively thick film of metallic materials for various microsystem applications. After learning about the material behavior of the electrochemically deposited Al, the next task is to develop a molded deposition and structural release process. The development of molded electrochemical deposition process allows the material to be deposited selectively only on the desired area. To extend the utilization of the electrochemically deposited Al film, in particular for microsystem applications, a microstructure formation by molded process from the chloroaluminate ionic liquid was investigated. The influences of each deposition parameters to the electrochemical deposition process as well as the resulting surface morphology were evaluated. Molded electrochemical deposition of Al on Au, Pt and Al seed layers were studied. The deposition on Al seed layer was possible by applying a reverse current before

starting the deposition. Such a reverse current helped to dissolve the native oxide existing in the surface, thus releasing a pure Al surface on the seed layer for Al electrochemical deposition, which was indicated by electrical potential monitoring. The availability of molded Al electrochemical deposition process was confirmed using 2 commercially available photoresist molds: negative tone AZ 125NXT and positive tone AZ P4620. Structures of 25  $\mu\text{m}$  width and over 15  $\mu\text{m}$  height was deposited, i.e. over 0.5 aspect ratio. Deposition on a microstructured substrate was also demonstrated. The deposited structures had a 10–100% larger dimension in comparison to the design, which can be attributed to the photoresist mold and should be considered for real device application. To form a suspended structure, a  $\text{SiO}_2$  deposited by a tetraethyl orthosilicate (TEOS) chemical vapor deposition (CVD) method was used as a sacrificial layer. Despite the structural imperfections, there was no obvious observed damage on the structure due to the vapor HF release process, which proved the feasibility of the fabrication of suspended structures using the proposed process. In addition, no obvious structural deformation was observed due to the residual stress of the material.

The applications of the electrochemical deposits can be generally categorized into 2: as a structural material or a packaging feature. As a structural material, Al has a superior coefficient of thermal expansion (CTE) in comparison to the other conventional materials. In addition, the electrochemically deposited Al film has shown a fine columnar shape of the grain, which yields a high electrical resistivity in the in-plane direction. Such features make the film suitable as a structural material of a thermal actuator. The large CTE can enhance the working displacement and force of the thermal actuator, while the high resistivity benefits to facilitate the Joule heating during the operation of the thermal actuator. Thermal actuator is usually useful in a microsystem to provide a large working force or displacement using a conventional material. Its working principle is based on the Joule heating of the structure upon electrical potential or current application and the thermal expansion phenomena. In this study, a linear and a bent-beam MEMS thermal actuator using an electrochemically deposited thick Al were fabricated. The thermal actuation of the linear thermal actuator by Joule heating and thermal expansion with the structure was confirmed. The power consumption at 0.8 A actuation current was 0.71 W. The temperature coefficient of resistivity (TCR) of the fabricated structure in between the temperature of 20°C to 30°C was measured to be  $0.007 \text{ K}^{-1}$ , which is twice the typical value for Al thin films. Such a high value also supports the Joule heating power generation in the structure. A maximum temperature of 60°C at a 2 V actuation potential was observed in the device, which yielded a 5.6  $\mu\text{m}$  displacement. The maximum displacement of the fabricated thermal actuator was as high as 10  $\mu\text{m}$  at a 3 V actuation voltage. The behavior was consistent with the finite element method simulation. The demonstration can open up a new class of MEMS thermal actuators using electrochemically deposited Al films as the structural material.

In the packaging spectrum, Al has a great potential as a wafer bonding material due to its inherent compatibility with the complementary metal oxide semiconductor (CMOS) processes. Wafer bonding technology has been a promising approach to

reduce the overall footprint of microdevices, providing heterogeneous device integration and hermetic packaging simultaneously. However, Al readily forms a native oxide layer upon exposure to the environment. Such a native oxide layer often prevents the atomic interdiffusion between the bonding layers, requiring a high temperature of typically around 450–500°C to be penetrated through. However, high bonding temperature caused thermal expansion of the structural material, and the difference of CTE can translate to different magnitude of expansions, which is often the source of cracks and failures. Therefore, the main challenge for Al based wafer bonding has been to reduce the wafer bonding temperature. In this study, a novel wafer bonding technique for heterogeneous integration using electrochemically deposited Al bonding frame was demonstrated. The Al bonding frames were deposited by electrochemical deposition from the chloroaluminate ionic liquid. The electrochemically deposited Al bonding frames were mechanically deformed by the groove structures on the counter wafer, i.e. marking press. A high localized pressure by the groove structure at the counter wafer caused a large mechanical deformation, which can also be utilized to intentionally break the native oxide of the electrochemically deposited bonding frame. Such a large mechanical deformation has enabled the wafer bonding at a temperature of as low as 250°C, which is the lowest value that has ever been reported for the Al bonding with the absence of any additional passivation layer or impurity. The influence of the bonding temperature and corner design to the quality of the bonded substrates were evaluated. The bonding shear strength of 4–100 MPa was obtained, which is in par with the other established techniques.

Finally, this study has provided a thorough investigation in paving the way to implement an electrochemically deposited Al film in microsystems. The revealed knowledge can open up a new class of microsystem technology based on the film. The future potential applications of the film in the microsystem field have been also presented.